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[54] POLLUTION CONTROLLED POLYSULFIDE RECOVERY PROCESS

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[52] **U.S. Cl.** **162/30**, 23/48, 162/60

[51] **Int. Cl.** **D21c 11/04**

[58] **Field of Search** ..... 162/29, 30, 38, 4 J, 60; 23/48, 49, 181, 186, 150

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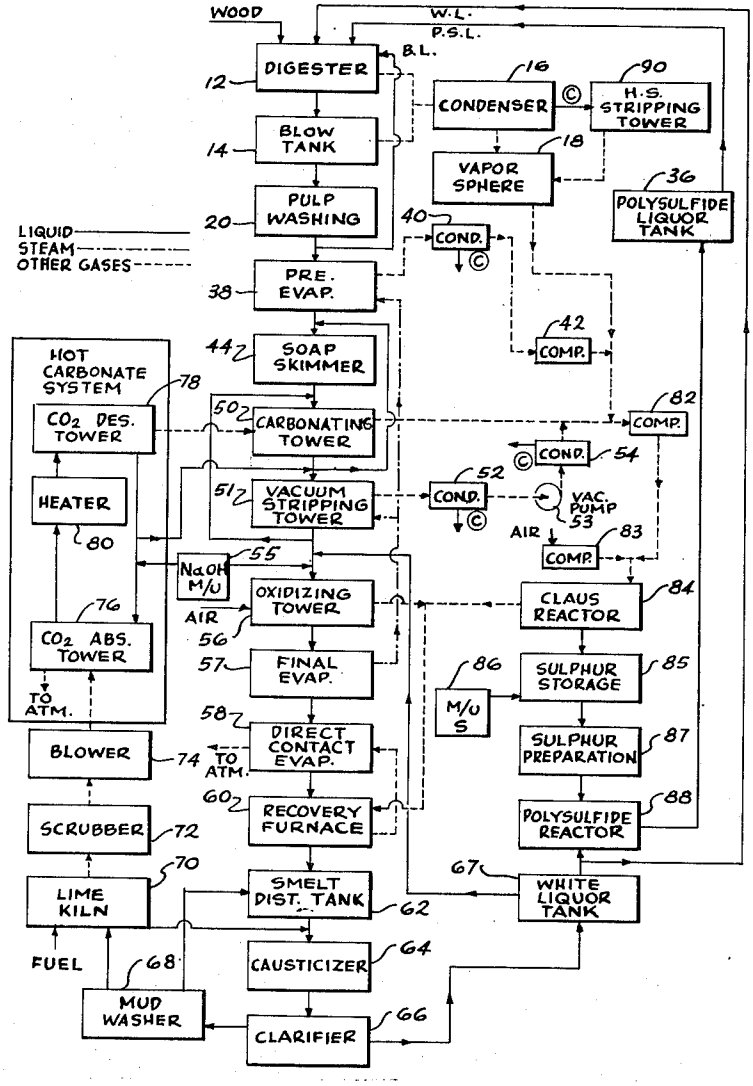
[57] **ABSTRACT**

A chemical recovery process for a polysulfide paper pulping system is described. After the polysulfide digestion, the pulp washing is carried out in an essentially oxygen-free environment to minimize the oxidation of NaSH. The spent liquor is pre-evaporated and mixed with a recycle stream of liquor containing Na_2CO_3 and $NaHCO_3$. The mixture is next carbonated with a gas stream rich in CO_2 which has been generated from lime kiln flue gas. The carbonated spent liquor is then vacuum stripped to release H_2S which is converted to sulfur. The sulfur is mixed and reacted with Na_2S in at least part of the white liquor to form sodium polysulfide. The polysulfide liquor and any remaining white liquor are returned to the digester.

The pH of the desulfurized liquor from the vacuum stripping operation is increased to about 12.5 by the addition of make-up NaOH and recycled and oxidized white liquor. The resulting mixture is then evaporated to about 50 percent dry solids concentration. Finally, direct contact evaporation and combustion of the spent liquor occur as in conventional kraft chemical recovery systems. Means for recovering all sulfur compounds in vent gases and condensates from all mill process unite such as the digesters, evaporators, lime kiln, etc., are included to reduce air and water pollution.

22 Claims, 4 Drawing Figures



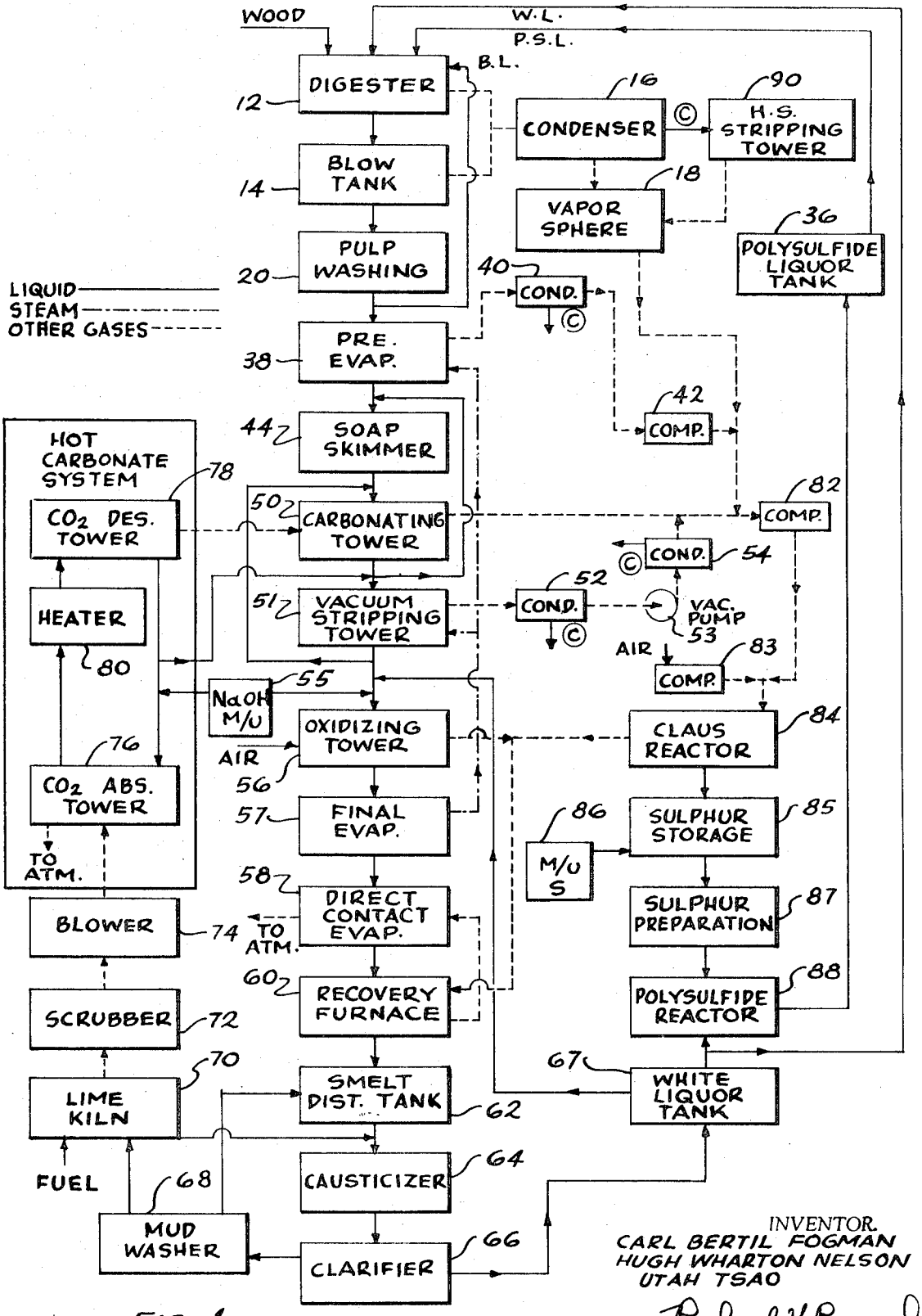


FIG-1

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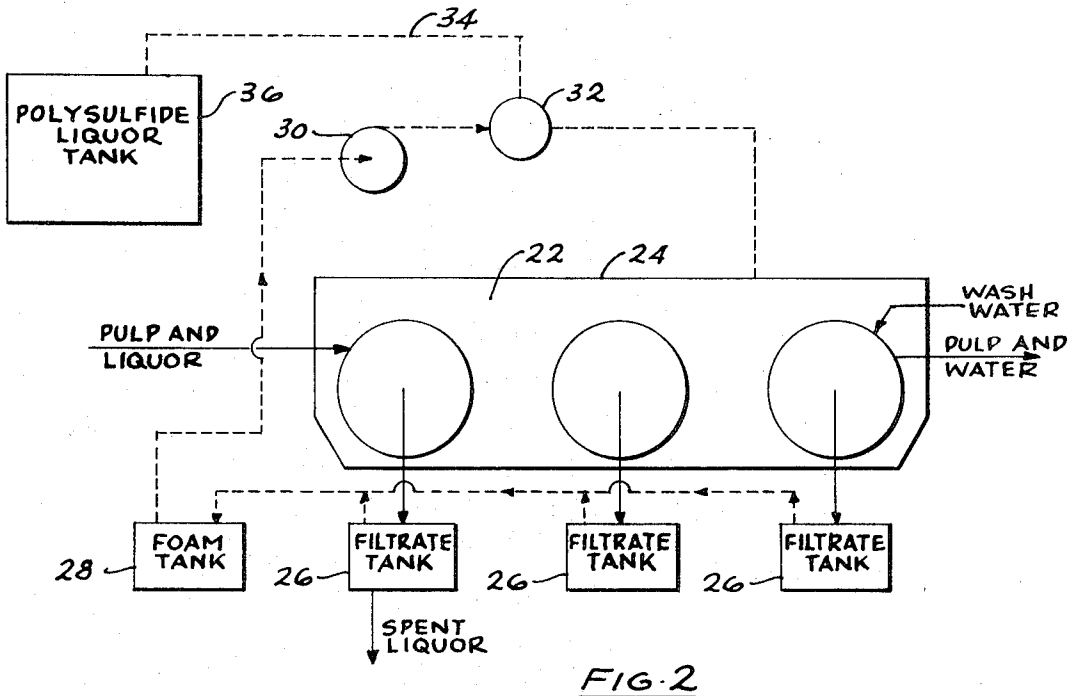

FIG. 2

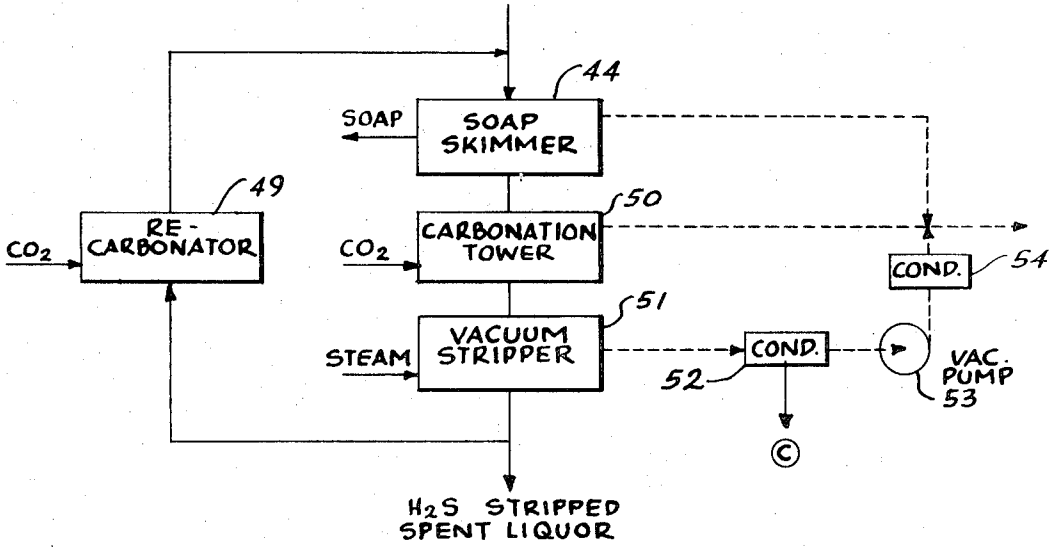

FIG. 4

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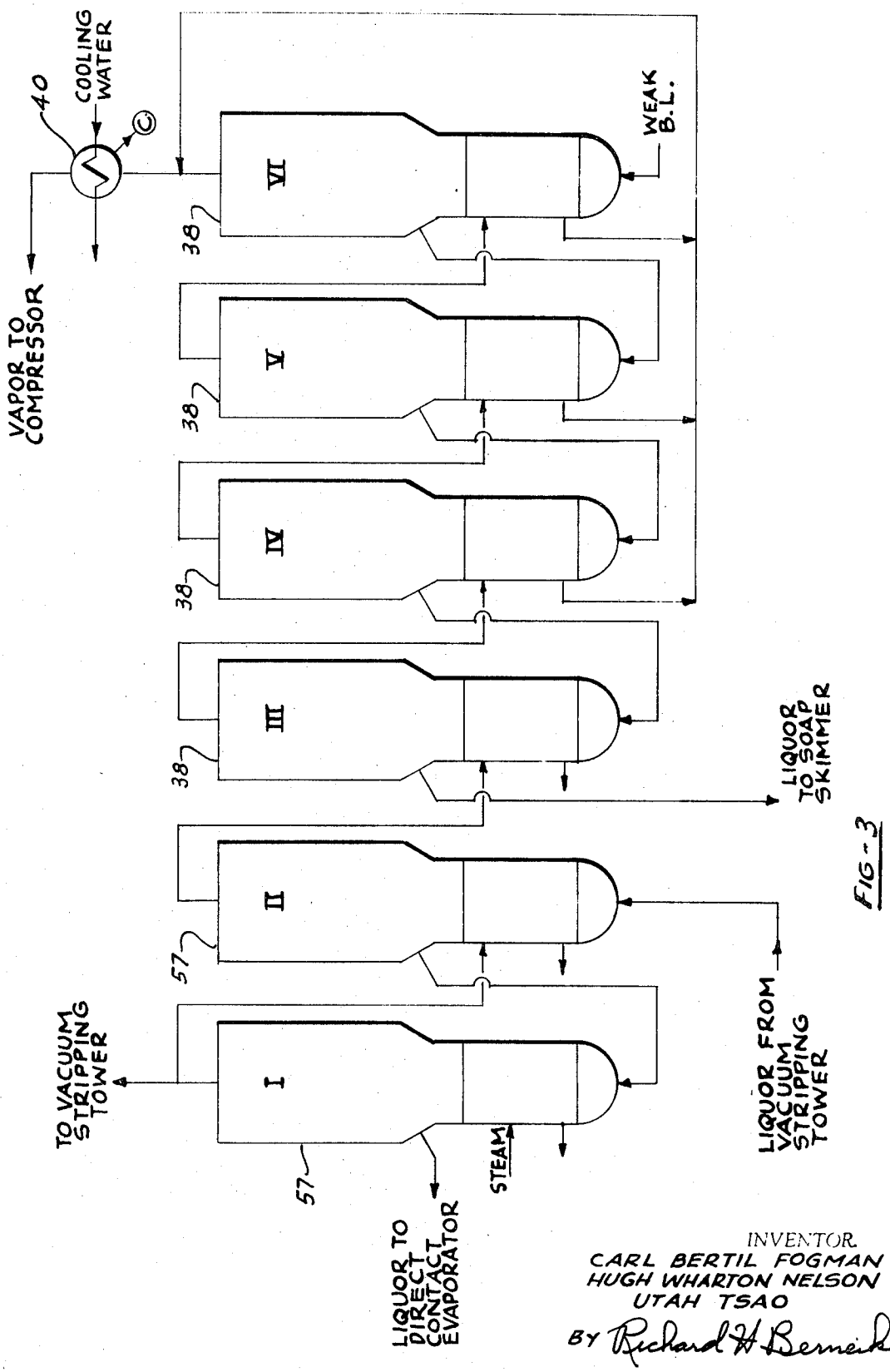

FIG-3

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POLLUTION CONTROLLED POLYSULFIDE RECOVERY PROCESS

BACKGROUND OF THE INVENTION

The pulping of wood by the polysulfide process is a known process that has been given much attention in recent years due to the higher yield of pulp from wood than obtained with the conventional kraft pulping process at the same pulp quality. Kraft pulping is done with an aqueous solution containing NaOH and Na_2S. In polysulfide pulping, sulfur is added to the same type of cooking liquor under conditions permitting the formation of sodium polysulfide, Na_2S_x. The improvement in pulp yield over the conventional process is on the order of 10 to 14 percent and since raw wood is the major cost item in pulp production, the economic incentives to develop the process are obvious.

The initial sulfur charge in polysulfide pulping may be more than three times higher than that of kraft and the spent liquor cannot undergo normal kraft evaporation and combustion without serious consequences. As examples, there would be an intolerable level of H_2S release in the mill operation causing an air and water pollution problem and there would also be increased corrosion and decreased capacity in the multiple-effect evaporators. Also, there would be increased corrosion problems in the chemical recovery furnace as well as increased explosion hazards due to the high sulfidity. These problems plus sulfur losses would make the system impractical.

SUMMARY OF THE INVENTION

The present invention is therefore directed to a practical chemical recovery system for use with polysulfide pulping. An object of the invention is to remove sulfur from the spent liquor prior to combustion in a chemical recovery furnace and to use this sulfur for producing fresh polysulfide cooking liquor. A further object is to prevent as much sulfur loss as possible thus preventing air and water pollution. These and other more detailed objects which will be more fully explained hereinafter are accomplished at least in part by means of the following process features.

The pulp washing after digestion is carried out so as to minimize the oxidation of NaSH which minimization is necessary to maximize sulfur recovery. The spent liquor is then pre-evaporated and mixed with a recycle stream containing $NaHCO_3$ and Na_2CO_3 so as to bring up the bicarbonate concentration to lower the pH for soap skimming and to bring up the carbonate concentration for the carbonation and H_2S stripping steps. Carbonation of the spent liquor to form the bicarbonate results in some H_2S release. The bulk of the H_2S release takes place in the subsequent vacuum stripping step to produce a concentrated H_2S stream for conversion to elemental sulfur for the production of polysulfide cooking liquor. Other features of the invention include controlling the concentration and pH so as to minimize or avoid process difficulties and recovering sulfur-containing gas or liquid streams which otherwise might cause pollution. These and other objects and advantages will be more apparent from the detailed description which follows.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is an overall process flow diagram.

FIG. **2** is a flow diagram of the pulp washing portion of the system.

FIG. **3** is a flow diagram of the multiple-effect evaporator system.

FIG. **4** is a flow diagram of an alternate liquor recycle arrangement.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Digestion

Wood chips such as loblolly pine ships, polysulfide liquor and white liquor are fed to the digester **12** along with any recycled spent back liquor necessary for fill. The preferred amount of polysulfide sulfur in the cooking liquor mixture amounts to about 4 percent by weight (dry basis) of the wood. The maximum practical amount of polysulfide sulfur is about 7 percent and the invention is operable to any amount of polysulfide up to this maximum. The polysulfide digestion process may be carried out either in a batch or continuous type operation. The digestion products are fed to a blow or flash tank **14** in which vapors are released. The vapor streams from both the digester **12** and the blow tank **14** contain sulfur compounds primarily in the form of hydrogen sulfide and mercaptans. The quantity of released sulfur compounds would be considerably higher than for a kraft digestion process. These vapors are thereafter fed to one or more condensers **16** where condensibles are removed and then to a vapor sphere **18** for storage and further processing.

Pulp Washing

In conventional kraft processes, the pulp undergoes a countercurrent washing operation to obtain a clean pulp product and a spent liquor at a relatively high concentration of dissolved nonpulp wood fractions and used chemicals. This washing is generally done in a three- or four-filter drum system having an open exhaust hood for vapor outlet which permits air entry. The liquor in a pulp washer contains a considerable amount of NaSH. In an open hood washing operation, a substantial amount of this NaSH is oxidized to $Na_2S_2O_3$. This is desirable in a kraft process since it fixes part of the sulfur in a nonvolatile form which does not produce H_2S in the evaporators downstream. The liquor coming from a polysulfide pulp process contains two to three times more NaSH than in the case of the kraft process. The successful operation of the present polysulfide sulfur recovery system requires that the amount of NaSH which is oxidized to $Na_2S_2O_3$ be minimized. Otherwise, an unreasonably high amount of Na_2S would have to be present in the cooking chemicals in order to obtain sufficient NaSH for conversion to H_2S and subsequently to sulfur, since the $Na_2S_2O_3$ remains intact during the disclosed process and does not contribute to H_2S formation.

Therefore, the present invention employs a pulp washing system **20** as illustrated in detail in FIG. **2**. This system includes a pulp washer **22** which is illustrated as having three filter drums. This pulp washer is totally enclosed by the hood **24** to essentially avoid any air infiltration. The filtrate from the drum washers is fed to individual filtrate tanks **26** in a countercurrent operation and the spent liquor discharged to the next operation as will be described hereinafter. The vapors from the filtrate tanks are fed to a foam tank **28** and then recycled by means of the blower **30** through vapor surge tank **32**. As also illustrated in FIG. **2**, the vapor surge tank **32** is connected by means of the surge line **34** with the polysulfide liquor tank **36**. This is for the purpose of blanketing the polysulfide liquor in its storage tank with nitrogen and water vapor to prevent oxidation of polysulfide to inactive thiosulfate.

This totally enclosed pulp washing system would have to operate for an initial short period (1 – 2 hours) to exhaust the oxygen inventory of the washing system. The oxygen would be exhausted by reacting with some of the NaSH present during this initial period. After this period, the vapor would be essentially nitrogen and water vapor thus preventing further oxidation.

A secondary beneficial effect of enclosing the pulp washer is a reduced heat consumption. Generally hot water at 55°–60° C. is fed to the last filter drum as wash water. With an open hood design, flash evaporation of water from the liquor occurs which keeps the temperature of the filtrate liquor leaving the first filter drum at about 85° C. At higher temperatures, the barometric leg suction principle applied to this type of washing operation would not function. With the totally enclosed system, such evaporation and heat loss would not occur. Therefore, in order to keep the temperature of the discharged spent liquor from going above 85° C., the wash water tempera-

ture must be reduced to about 35°–40° C. A further advantage of the enclosed washing system is the elimination of H_2S discharge to the atmosphere such as occurs in an open system. An additional benefit to be realized from enclosing the pulp washer is that the brightness of the pulp would be increased. The lignin still remaining undissolved in the pulp, if oxidized in the presence of black liquor results in a reduction of the brightness. Elimination of oxygen prevents this from occurring and increases the pulp brightness.

Pre-evaporation

The spent liquor from the pulp washing operation **20**, after any necessary portion has been recycled to the digester **12**, is fed to the pre-evaporators **38** which may consist, for example, of the last four stages of a six-stage multiple-effect evaporator system. The purpose of evaporation in a pulp mill chemical recovery system is to concentrate the organic and inorganic constituents so that the liquor may be burned in the chemical recovery furnace. The purpose of the pre-evaporation step at this point in the present invention is to create optimum conditions for two subsequent steps in the polysulfide sulfur recovery process, namely CO_2 absorption and H_2S stripping. This pre-evaporation concentrates the NaSH and Na_2CO_3 which increases the kinetics of the subsequent processing steps and reduces the size of the necessary equipment. Also, soaps can be effectively separated from the spent liquor after it has been pre-evaporated to 25–30 percent dry solids. This soap separation facilitates the following processing steps because of lessened foaming tendencies. The pre-evaporation also gives a relatively high liquor specific gravity, 1.12–1.15, and reasonably low viscosity, about 2 centipoise. The higher specific gravity results in the easier collapse of any foam that is generated and the viscosity of low enough for obtaining good chemical mass transfer in the CO_2 absorption and H_2S stripping operations.

The pre-evaporation as well as the final evaporation sections are shown in more detail in FIG. **3**. The function of the final evaporation section in the overall process will be described in more detail hereinafter. The weak black liquor from the pulp washing system **20** at a concentration of about 15–18 percent dry solids is fed to Stage VI of the countercurrent flow, multiple effect evaporator system. The vapor from this Stage VI, which contains some H_2S, is fed to a condenser **40**. The condensate C from the condenser is fed to a condensate treating system which will also be described hereinafter. The vented vapors from the condenser **40** are fed to a compressor **42** as indicated in FIG. **1**.

Stages III through VI of the multiple effect evaporators are employed in the pre-evaporation section. The liquor flows from Stage VI to Stage V to Stage IV to Stage III and then out of the evaporator system to the soap skimmer **44** at a concentration of 25–30 percent dry solids. The vapors in the pre-evaporation section flow from Stage III to IV to V and then to Stage VI. Minor continuous vapor purge from the steam chests of Stages IV, V, and VI are made to release H_2S through the lower part of the steam chests of the evaporator bodies. The effluent from these steam chests is conducted to condenser **40** with the condensate being fed to the above-mentioned condensate treating system and with the H_2S-containing vented vapors being fed to compressor **42** along with the vapors from Stage VI. The compressor **42** is used for receiving the vented vapors from the condenser **40**.

Improved Soap Skimming and Recycle

The effluent from Stage III of the pre-evaporation section is fed to a conventional soap skimmer **44** which provides approximately one hour dwell time as in normal skimming operation. The 25–30 percent dry solids concentration of this feed to the soap skimmer is most favorable to such a skimming operation. It has been found, however, that the normal soap skimming operation can be greatly improved by recycling a quantity of liquor rich in $NaHCO_3$ from the subsequent carbonation step as shown in FIG. **1**. This recycle has two beneficial effects. Firstly, the $NaHCO_3$ lowers the pH which enhances soap separation. Secondly, the $NaHCO_3$ reacts with NaSH forming H_2S bubbles, which facilitate flotation of soap to the surface. The amount of carbonated liquor recycled is adjusted to obtain the necessary soap separation. It has been found that a recycle of between about 50 and 200 percent of the incoming main liquor stream is a suitable range with about 100 percent recycle being preferred.

An alternate recycle scheme is illustrated in FIG. **4**. In this arrangement, the recycle is H_2S stripped liquor taken from the vacuum stripper rather than carbonated liquor from the carbonating tower. This recycle is passed through a recarbonator **49** in which Na_2CO_3 is converted to $NaHCO_3$. The CO_2 supply to the recarbonator **49** may be a 100 percent CO_2 stream (dry basis) such as from a hot carbonate system, which will be described hereinafter, or it may be a flue gas stream such as from a lime kiln. This recarbonation step provides the $NaHCO_3$ in the recycle stream necessary for effective soap skimming as described above.

The soap skimming operation in the present invention has several advantages. IN passing spent liquor containing soaps through a packed column, there is a tendency for the soaps to coat the packing material. This soap coating forms a sticky surface to which the precipitated lignin readily adheres. This can very rapidly cause the packed column to plug. Effective soap removal can essentially eliminate this problem. Another problem which occurs when soaps are present in spent liquor is foaming in various operations such as gas-spent liquor contact steps including carbonation, stripping, and oxidation. This foaming problem can also be reduced by means of the improved soap skimming operation. A third benefit of the improved soap skimming is that the soap yield and consequently the tall oil yield if significantly increased.

Carbonation and Recycle

Following soap skimming, the main liquor stream is passed to the carbonating tower **50** wherein CO_2 is reacted with Na_2CO_3 to produce $NaHCO_3$ according to the following reaction:

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3 \quad (1)$$

The H_2S stripping step, which will be explained hereinafter involves a reaction of this $NaHCO_3$ with NaSH to form H_2S according to the following reaction:

$$NaSH + NaHCO_3 \rightarrow H_2S + Na_2CO_3 \quad (2)$$

The following side reaction occurs simultaneously in the vacuum stripping tower:

$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O \quad (3)$$

This means that there must be sufficient Na_2CO_3 present in the feed to the carbonating tower to subsequently provide sufficient $NaHCO_3$ for the two latter reactions. Since the spent liquor feed to the carbonating tower may not contain enough Na_2CO_3 for this purpose, a quantity of spent liquor from the subsequent H_2S stripping step which is rich in Na_2CO_3 can be recycled and introduced into the carbonating tower **50** along with the main liquor stream. The amount of recycle is selected such that the mole ratio of $NaHCO_3$ to Na_2CO_3 at the end of the carbonating step will be at least 7.5 and the mole ratio of $NaHCO_3$ to NaSH will be about 1.5 – 2.5. Depending upon the amount of Na_2CO_3 in the incoming liquor stream to the carbonation tower **50**, this recycle may be anywhere from 0 – 100 percent of the quantity of liquor coming from the pre-evaporation section. When these conditions exist, there will be sufficient $NaHCO_3$ available to permit the subsequent stripping of H_2S and CO_2 according to reactions (**2**) and (**3**) above.

The CO_2 gas stream fed to the carbonating tower **50** is preferably 100 percent CO_2 (dry basis) at about the tower operating pressure and temperature. This pure CO_2 gas stream is obtained from a hot carbonate system which will be described hereinafter and it is passed countercurrent to the downcoming liquor stream. It is desirable that only enough CO_2 be passed through the carbonating tower **50** to produce the desired amount of $NaHCO_3$. The fact that the CO_2 stream is concentrated and thus small, in terms of gas flow, means that the amount of H_2S released in the carbonating tower will be small because of its partial pressure/vapor pressure rela-

tionship. The partial pressure of CO_2 in the gas passing through the CO_2 absorbing tower will at all times be greater than the CO_2 vapor pressure which means that there will always be a driving force causing the mass transfer of CO_2 from the gas to the liquid. With a lean CO_2 gas stream, such as the flue gas from a lime kiln, the H_2S stripping rate in the carbonating tower would be much higher. The discharge would be a gas stream lean in H_2S. But the purpose of this invention is to create a mixture of gases from the carbonating tower, the H_2S stripping tower and other sources so rich in H_2S as to permit an efficient operation of the Clause reactor **84**.

The amount of CO_2 fed to the carbonating tower should be as follows:

$$\frac{CO_2 \text{ in the gas feed}}{NaSH \text{ in the liquor feed}} = 0.5 - 4.0 \text{ (preferably } 1 - 2)$$

expressed as molar ratio.

Although the carbonating tower **50** may operate, for example, at a pressure anywhere from atmospheric to 100 p.s.i.a. and at a temperature from 25°–100° C., a more practical range is atmospheric pressure to 30 p.s.i.a. and 50°–80° C. As the temperature is increased, the partial pressure of CO_2 decreases and the vapor pressure of the CO_2 increases so that the pressure differential from the gas to the liquid would become nil. The temperature should also not get too low since the liquor becomes too viscous and the reaction rates become too low. The overhead vapor stream from the carbonating tower **50** containing excess CO_2 and some H_2S is combined with the vent from condenser **54**, the discharge from compressor **42**, and the vapor sphere discharge stream as part of the feed to the Claus reactor **84**.

H_2S Stripping

A portion of the carbonated liquor stream discharged from the carbonating tower **50** is recycled to the soap skimmer **44** as discussed hereinbefore. The remaining carbonated liquor stream is fed to the vacuum stripping tower **51** together with a bleed stream from the hot carbonate system which will be explained hereinafter. This bleed stream contains sodium carbonate and bicarbonate (approximately 12 to 15 percent) and a small amount of Na_2SO_3 (approximately 5 to 6 percent). The bleed stream can also be introduced before the carbonating tower **50**.

The stripping tower **51** is a packed column in which the bicarbonated liquor undergoes vacuum steam stripping whereby H_2S and some CO_2 are released. Any other type of equipment conventionally used for gas stripping may be used in place of the packed column. The stream for carrying out this stripping operation is obtained, for example, from Stage I of the multiple effect evaporator system as indicated in FIG. **3** or from stages II or III. The primary reaction that occurs is:

(2) $NaSH + NaHCO_3 \rightarrow Na_2CO_3 + H_2S$

This would require one mole of $NaHCO_3$ for one mole of NaSH but there is a competing side reaction:

(3) $2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$

This side reaction requires that additional $NaHCO_3$ be present and furthermore, a residual amount of $NaHCO_3$ must be present as a chemical driving force according to the following equilibrium equation:

$$vp_{H_2S} = K \frac{(HCO_3^-)(SH^-)}{(CO_3^=)}$$

At constant K and (SH^-), the higher the ratio of bicarbonate to carbonate, the higher the vapor pressure of H_2S over the liquid to be stripped. The liquor temperature in the stripping tower will be at or below the boiling point of the liquor at the tower pressure. The vacuum stripping tower may operate, for example, at a pressure anywhere from about 5 in. Hg absolute up to atmospheric pressure. A more practical range is 8–17 in. Hg absolute with the preferred pressure being about 10 in. Hg absolute. The overhead vapor stream from the stripping tower is condensed to overhead condenser **52**, compressed by vacuum pump **53** to atmospheric pressure, fed to condenser **54** and then fed to the sulfur recovery system along with other vented vapor streams.

Chemical Makeup

The makeup chemical in a kraft mill is generally Na_2SO_4 in which the ratio of sodium and sulfur losses (Na_2:S) is equal to one. In the polysulfide pulping and recovery system, the sulfide sulfur contained in all liquor streams is substantially higher than in the case of kraft. In order to abate the emission of sulfur compounds, practically every vapor and condensate stream is captured and elemental sulfur recovered for reuse in the process resulting in a chemical loss ratio (Na_2:S) of about 1.4. To achieve pollution and chemical process control as described hereinafter, sodium hydroxide is used as a makeup for sodium losses and is added to the main liquor stream after the H_2S stripping step. Makeup sulfur is added to the elemental sulfur stream after Claus reactor **84** as explained hereinafter. Therefore, the sulfidity of smelt from the recovery boiler is kept at a low level reducing the odor and smelt explosion problems from this particular unit.

The liquor coming from the stripping tower **51** has a pH of about 10.0–10.5 and the addition of NaOH will increase the pH. However, the amount of NaOH added for sodium makeup reasons may not be sufficient to increase the pH to a range in which the precipitated lignin will be dissolved and kept in solution through the subsequent evaporation steps. Otherwise, lignin precipitate would foul the surfaces of the evaporators. Therefore, in order to increase the pH to the desired range of 12–13, a quantity of white liquor is recycled as shown in FIG. **1**. This increased pH will also prevent the release of H_2S in the following direct contact evaporation step.

The amount of white liquor recycled and the exact pH desired will depend primarily upon the type of direct contact evaporator which is used. If the evaporating gas stream is hot flue gas, which contains CO_2 that lowers the liquor pH, it will be necessary to add more white liquor to give a higher initial pH. If hot air is used in the direct contact evaporator, in which case the pH will not be lowered, less white liquor can be recycled and perhaps the recycle can even be eliminated.

Oxidation

The recycle of white liquor as described above will introduce some Na_2S into the black liquor stream in addition to whatever residual Na_2S might be present. This Na_2S may be partially converted to H_2S in a flue gas direct contact evaporator and as such would be released to the atmosphere as a pollutant. Therefore, the black liquor, after the white liquor addition is subjected to a low level oxidation step in which the Na_2S is oxidized to the stable $Na_2S_2O_3$. This step is carried out with air or oxygen in the oxidizing tower **56** which may be a packed tower or any other suitable form of liquid gas contactor. Black liquor oxidizers have been used in the past but with soap-containing liquors they have failed due to foaming. In the present invention, however, the soaps have been removed and foaming is no longer a serios problem. air from the oxidizing tower **56**, which may contain some sulfur compounds, is incinerated in the recovery boiler as shown in FIG. **1**.

Final Evaporation

The H_2S stripped liquor after mixing with the makeup NaOH and any necessary white liquor recycle and after oxidizing tower **56** is then fed to Stage II of the multiple-effect evaporator system as shown in FIG. **3**. The final evaporators **57** increase the concentration of the liquor up to 50–55 percent dry solids. The vapors from Stage II of the final evaporation section are used to heat Stage III of the pre-evaporator section while the vapors from Stage I of the final evaporation section are used both to heat Stage II and to feed the vacuum stripping tower **51** as previously mentioned.

Direct Contact Evaporation

The liquor discharged from Stage I of the final evaporation system is fed to a direct contact evaporator such as a conventional cascade evaporator in which water is evaporated from the liquor by direct contact with the flue gases from the recovery boiler. Another type of direct contact evaporator which can be used is the air cascade evaporator in which air, which has been heated by heat exchange with the flue gases, is used for the evaporation instead of flue gases. In this case, the liquor would not be contacted with the flue gas CO_2 and its pH

would not be lowered. Therefore, as described above, it might be possible to reduce or eliminate the white liquor recycle. With the air cascade evaporator, the oxidizing tower **56** can also be eliminated.

The liquor is concentrated in this evaporator from 50–55 percent to about 70 percent dry solids concentration producing a liquor suitable for burning. Due to the low content of NaSH and Na_2S in the liquor at this point and the high pH, the emission of H_2S from the direct contact evaporator by reaction with CO_2 will be close to nil. Under certain conditions H_2S discharged from the recovery furnace could be partially absorbed in this evaporator contributing to the reduction in air pollution by H_2S.

Recovery Furnace

The liquor from the direct contact evaporator is next fed to a conventional chemical recovery furnace **60** with steam boiler discharging a smelt consisting mainly of Na_2S and Na_2CO_3 and a flue has which generates steam in the boiler section of the furnace. The sulfidity of the smelt is about 25 percent, which is normal as compared to conventional kraft units. High sulfur-to-sodium ratio in the feed liquor to a chemical recovery furnace causes corrosion problems and greatly increases the chances of dangerous smelt-water explosions. A sulfidity of about 25 percent is significantly below the danger level. The flue gases from the chemical recovery furnace are used either directly or indirectly to carry out the evaporation in the direct contact evaporator as indicated above and in FIG. **1**.

Smelt Processing

The smelt from the chemical recovery furnace is handled in much the same manner as in the conventional kraft process. The smelt is dissolved in an aqueous solution in tank **62** producing what is commonly called the green liquor. The green liquor from the smelt dissolving tank together with calcium oxide from the lime kiln is then reacted in the causticizer **64** to form conventional white liquor which is then clarified at **66**. The white liquor from the clarifier is drained off into the white liquor storage tank **67** and a portion recycled to the H_2S stripped black liquor stream as needed and discussed above. The solid precipitate from the clarifier **66** containing mostly $CaCO_3$ is conducted to the washer **68** in which the $CaCO_3$ is washed. The wash water is then used to dissolve the smelt in tank **62**. The $CaCO_3$ from the washer is next fed to the lime kiln **70** in which the $CaCO_3$ is converted to CaO and CO_2. The CaO from the lime kiln **70** is then recycled to the causticizer **64**.

The gases from the lime kiln **70** containing primarily CO_2 and N_2 are passed to a wet scrubber **72** for the removal of particular matter and the major part of any SO_2 present and then passed by means of the blower **74** into the hot carbonate system. The hot carbonate system comprises a CO_2 absorption tower **76** and a CO_2 desorption tower **78**. The absorbing liquor in the hot carbonate system is a mixture of $NaHCO_3$ and Na_2CO_3. The gases as discharged from the absorption tower **76** to atmosphere do not contain any H_2S or SO_2 thus eliminating this pollution problem. The liquor from the absorption tower **76** is then sent via a heater **80** to the CO_2 desorption tower **78** in which CO_2 is stripped off the bicarbonate/carbonate mixture at a temperature of about 220–230° F. This desorption tower has a reboiler at the bottom to furnish the necessary heat for the stripping operation. The liquor from the desorption tower, which is then cooled, is recycled to the absorption tower **76**. The overhead vapor from the desorption tower **78** contains 100 percent CO_2 (dry basis) and is used to feed the carbonating tower **50**. Since there will be a tendency to build up Na_2SO_3 and other matter in the hot carbonate system, a portion of the circulating liquor in this system is bled and fed to the carbonation tower **50** or the stripping tower **51** as previously discussed. Pure NaOH is used as makeup for the circulating liquor in the hot carbonate system as a replacement for the bleed stream.

Sulfur Recovery

The vapors from the vacuum stripping tower **51**, the carbonation tower **50**, the pre-evaporators **38** and the vapor sphere **18** are mixed as shown in FIG. **1**. The mixture containing about 50 percent H_2S and 50 percent CO_2 by volume is further compressed at **82**. The gas from the compressor **82** is passed to a reactor **84** in which the hydrogen sulfide is converted to elemental sulfur. This conversion may be accomplished by any one of the many processes available. One such process is the well-known Claus reaction, a gas phase, catalytic reaction, which takes place at relatively high temperature. The gas from the compressor **82** at a pressure of about 9 p.s.i.g. is combined with air also at 9 p.s.i.g. in the exact stoichiometric ratio and reacted in the Claus reactor as follows:

$$H_2S + 1\text{-}\tfrac{1}{2}\,O_2 \rightarrow SO_2 + H_2O \quad (4)$$

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O \quad (5)$$

The tail-end gases from the Claus reactor contain primarily CO_2 and N_2 but may contain some unreacted H_2S and SO_2. These gases are therefore sent as part of the air feed to the chemical recovery furnace for complete incineration of the H_2S and SO_2. At the temperatures prevailing in the zone of air introduction, volatilized Na_2O will combine with SO_2 to form Na_2SO_3. This will be further oxidized to Na_2SO_4 by the oxygen in excess air. This Na_2SO_4 is removed from the flue gases by the conventional electrostatic precipitator. The elemental sulfur from the Claus reactor is discharged to the sulfur storage **85**. The exothermix heat from the Claus reactions can be utilized for steam generation.

Polysulfide Production

The molten sulfur from the sulfur storage **85** together with molten makeup sulfur is subjected to cooling, prilling and crushing in the sulfur preparation section **87**. The sulfur is then metered along with the white liquor to the polysulfide reactor system **88** in which the mixture is circulated between a mixer and settler during which the sulfur is reacted with sodium sulfide in the white liquor to produce polysulfide according to the following reaction:

$$Na_2S + nS \rightarrow Na_2S_{n+1} \quad (6)$$

wherein "n" is normally 1–4, preferably 1.0–2.5. The amount of polysulfide produced in this conventional reaction will depend upon the various proportions of sulfur to white liquor and various operating conditions in the digester **12**. The polysulfide liquor is then fed to tank **36** for storage under oxygen-free blanket in preparation for use in pulping.

Pollution Control

Sulfur compounds are generated in a polysulfide pulp-producing mill at a rate five to six times larger than in a kraft mill. This requires that measures be taken to prevent air and water pollution. This is accomplished according to the present invention by collecting all such streams and recovering the sulfur compounds. For example, the gases from the digester **12**, the blow tank **14**, the pre-evaporators **38**, and the carbonating tower **50**, after removing the condensibles are sent to the Claus reactor **84** for the conversion of sulfur compounds into elemental sulfur. The condensates "C" from condenser **16, 40, 48, 52** and **54** are sent to a condensate recovery system which includes an H_2S stripping tower **90**. The combined condensate is heated and stripped at 212° F. with steam, yielding a sulfur-free reusable bottoms stream and an overhead vapor. This overhead vapor is condensed and the condensate is decanted yielding raw turpentine and water both containing sulfur compounds. The turpentine fraction can be sold as such on burned in the recovery boiler **60**, while the water fraction is recycled to the stripping tower. The vent leaving the condenser joins the digestion vents in the vapor sphere **18** for sulfur conversion in the Claus reactor **84**.

It can be seen from the above description of the invention that the problems associated with the chemical recovery of polysulfide spent liquor such as high sulfidity in the chemical recovery furnace, sulfur losses, and air and water pollution, have been overcome.

While the foregoing description has specifically referred to the production of pulp from loblolly pine, it will be apparent

that the present invention is fully applicable to the treatment of other cellulose fiber materials such as all the species of wood used in the pulp industry as well as the annual crops in the form of bagasse, straw and the like.

While preferred embodiments and alternatives of the invention have been shown and described, it will be understood that they are merely illustrative and that changes may be made without departing from the scope of the invention as claimed.

We claim:

1. A method of processing the NaSH- and Na_2CO_3-containing spent liquor from a polysulfide pulping process comprising the steps of:

a. washing polysulfide spent liquor from the digested pulp in a substantially oxygen-free atmosphere whereby oxidation of NaSH is minimized;

b. adding a recycle stream containing $NaHCO_3$ to said liquor thereby reducing the pH;

c. carbonating said spent liquor with CO_2 so as to convert Na_2CO_3 to $NaHCO_3$ whereby said $NaHCO_3$ will be present in an amount sufficient to react with substantially all of said NaSH to form H_2S;

d. vacuum stripping said H_2S from said spent liquor at a pressure below atmospheric;

e. increasing the pH of said stripped spent liquor to a level which will prevent lignin precipitation during subsequent processing including the step of adding NaOH for sodium makeup;

f. evaporating and processing said spent liquor to produce white liquor containing NaOH and Na_2S;

g. converting said H_2S to elemental sulfur; and

h. reacting said elemental sulfur with at least a portion of said white liquor to produce polysulfide cooking liquor.

2. A method according to claim 1 and further including the step of pre-evaporating said spent liquor subsequent to washing step (a) and prior to $NaHCO_3$ addition step (b).

3. A method according to claim 2 wherein said recycle stream containing $NaHCO_3$ added in step (b) is a recycle stream of carbonated spent liquor from step (c).

4. A method according to claim 3 and further including the step of adding Na_2CO_3 to said spent liquor prior to said carbonating step (c), said added Na_2CO_3 being contained in a recycle stream of vacuum stripped spent liquor from step (d).

5. A method according to claim 2 wherein said recycle stream containing $NaHCO_3$ added in step (b) is a recycle stream of vacuum stripped spent liquor from step (d) and further including the step of recarbonating said recycle stream to convert at least a portion of the Na_2CO_3 in said recycle stream to $NaHCO_3$.

6. A method according to claim 2 wherein said spent liquor is pre-evaporated to a dry solids content of 25–30 percent.

7. A method according to claim 6 wherein said carbonating step (c) takes place at a temperature of from about 25° to 100° C. and at a pressure of between about atmospheric pressure and 100 p.s.i.a.

8. A method according to claim 7 wherein said vacuum stripping step is carried out at a pressure of between about 5 in. Hg absolute and atmospheric pressure.

9. A method according to claim 8 wherein said carbonating temperature is from about 50° to 80° C. and said carbonating pressure is between about atmospheric pressure and 30 p.s.i.a.

10. A method according to claim 9 wherein said stripping pressure is between about 8 – 17 in. Hg absolute.

11. A method according to claim 1 wherein the step (e) of increasing the pH of said stripped spent liquor further includes the step of recycling a quantity of white liquor to increase the pH of said stripped spent liquor above the point attained by said NaOH addition.

12. A method according to claim 11 and further including the step of oxidizing Na_2S in said spent liquor subsequent to the step of recycling said white liquor and prior to step (f).

13. A method according to claim 1 wherein said carbonating step (c) comprises contacting said spent liquor with a gas stream which is substantially pure CO_2 on the dry basis.

14. A method according to claim 13 wherein said processing step (f) comprises concentrating said spent liquor by evaporation, burning said spent liquor to produce a smelt containing Na_2CO_3 and Na_2S and processing said smelt to produce said white liquor and additionally to produce a CO_2-containing gas stream and further including the step of processing said CO_2-containing gas stream to produce said substantially pure CO_2 for step (c).

15. A method of processing the spent liquor from a polysulfide pulping process wherein said liquor contains NaSH and Na_2CO_3 comprising the steps of:

a. separating the pulp from said liquor and conducting said liquor to a pre-evaporation stage while maintaining said liquor in a substantially oxygen-free atmosphere to minimize the oxidation of said NaSH;

b. pre-evaporating said liquor to about 25–30 percent solids;

c. adding a $NaHCO_3$-containing recycle stream to said liquor to lower the pH;

d. skimming soap from said liquor;

e. contacting said liquor with a CO_2-containing gas stream which is substantially pure CO_2 on the dry basis, so as to convert Na_2CO_3 to $NaHCO_3$ whereby said $NaHCO_3$ will be present in an amount sufficient to react with substantially all of said NaSH to form H_2S, said contacting step being carried out at a temperature of from about 50° to 80° C. and at a pressure of between about atmospheric pressure and 30 p.s.i.a. whereby said CO_2 and said Na_2CO_3 and said NaSH react to form said $NaHCO_3$ as well as a gaseous effluent containing a small quantity of H_2S;

f. subjecting said liquor to vacuum stripping whereby H_2S gas formed by reaction of $NaHCO_3$ with NaSH is separated from said liquor, said vacuum stripping being carried out at a pressure between about 5 in. Hg absolute and atmospheric pressure;

g. increasing the pH of said stripped spent liquor to a level which will prevent lignin precipitation during subsequent processing including the step of adding NaOH for sodium makeup;

h. concentrating said liquor by evaporation to produce a liquor capable of burning;

i. burning said concentrated liquor to provide a smelt containing Na_2CO_3 and Na_2S;

j. processing said smelt to produce a white liquor containing NaOH and Na_2S and to produce a CO_2-containing gas;

k. processing said CO_2-containing gas to provide said substantially pure CO_2 on the dry basis for step (e);

l. collecting the H_2S gaseous effluents from steps (b) and (e) and (f) and converting said H_2S to elemental sulfur;

m. reacting said elemental sulfur with at least a portion of said white liquor to produce polysulfide cooking liquor.

16. A method according to claim 15 and further including the step of adding a Na_2CO_3-containing recycle stream to said liquor subsequent to skimming step (d) and prior to contacting step (e).

17. A method according to claim 15 wherein said $NaHCO_3$ recycle added in step (c) is a recycle stream of vacuum stripped liquor from step (f) and further including the step of recarbonating said recycle stream to convert at least a portion of the Na_2CO_3 in said recycle stream to $NaHCO_3$.

18. A method according to claim 15 wherein said step (l) further includes collecting the gaseous effluents containing sulfur compounds from other of said processing steps and converting said sulfur compounds to elemental sulfur.

19. A method according to claim 1 and further including the step of separating soap from said spent liquor.

20. A method according to claim 19 wherein said soap is separated from said spent liquor subsequent to $NaHCO_3$ addition step (b) and prior to said carbonating step (c).

21. A method according to claim 1 wherein said mole ratio of $NaHCO_3$ to NaSH subsequent to carbonating step (c) is about 1.5 to 2.5.

22. A method according to claim 21 wherein the mole ratio of the CO_2 employed in carbonating step (c) to the amount of NaSH in the liquor is about 0.5 to 4.0.

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